

COMPOSITION COMPRISING A SEMI-CRYSTALLINE POLYMER AND  
AN ESTER

The present invention relates to a composition, particularly a cosmetic composition,  
5 comprising at least one semi-crystalline polymer and an ester, which is in the form in particular of a stick which is smooth on application and which leads to a glossy and comfortable coating.

Cosmetic compositions whose fatty phase is  
10 gelled using semi-crystalline polymers have been described in the as yet unpublished application FR 0106047. The lipstick formulas resulting from these inventions are in the form of a stick which lays down a glossy film which is not sticky and provides good  
15 coverage. These compositions, however, have the drawback of not going on easily when they are applied to keratin materials.

It is therefore an aim of the present invention to provide a composition comprising a liquid  
20 fatty phase structured with a semi-crystalline polymer having an organic structure, which is solid at ambient temperature, the coating of which composition on the skin or lips is glossy and comfortable, and which is easy to apply.

25 Patents US 5 736 125 and US 5 156 911, and also application WO 01/19333, illustrates certain types of semi-crystalline polymers which may form part of the

composition of the formulas of the invention. These documents, nevertheless, do not describe cosmetic compositions.

Surprisingly the applicant has found that the  
5 addition of an ester containing 10 to 40 carbon atoms to a composition comprising a semi-crystalline polymer allows the coating of the composition to be improved and its gloss to be enhanced.

The invention applies in particular to lip  
10 makeup products but also to eye makeup products, such as eyeliners, in particular in pencil form, and mascaras, in particular in block form, or skin makeup products, such as foundations.

More specifically the invention provides a  
15 makeup composition comprising a) at least one liquid fatty phase structured with at least one semi-crystalline polymer having an organic structure and a melting temperature of greater than or equal to 30°C, b) a colorant and c) an ester containing 10 to 40 carbon  
20 atoms, the liquid fatty phase, colorant, ester and polymer forming a physiologically acceptable medium.

The melting temperature of the semi-crystalline polymer is preferably less than 150°C.

The composition of the invention may be in  
25 the form of a paste, a solid or a cream. It may be an oil-in-water emulsion or a water-in-oil emulsion, or a solid or soft anhydrous gel. It is preferably in

anhydrous form, and more especially in the form of an anhydrous gel, especially cast as a stick or as a dish.

For the purposes of the invention, the term "semi-crystalline polymer" means polymers comprising a  
5 crystallizable portion and an amorphous portion in the skeleton and having a first-order reversible change of phase temperature, in particular of melting (solid-liquid transition). The crystallizable portion is either a side chain (or pendent chain) or a block in  
10 the skeleton.

For the purposes of the present invention, the term "polymers" means compounds containing at least 2 repeating units, preferably at least 3 repeating units and more especially at least 10 repeating units.

15 When the crystallizable portion is a block of the polymer skeleton, this crystallizable block has a different chemical nature to that of the amorphous blocks; in this case, the semi-crystalline polymer is a block copolymer, for example of the diblock, triblock  
20 or multiblock type. When the crystallizable portion is a chain that is pendent on the skeleton, the semi-crystalline polymer may be a homopolymer or a copolymer.

The terms "organic compound" and "having an  
25 organic structure" mean compounds containing carbon atoms and hydrogen atoms, and possibly heteroatoms such as S, O, N or P, alone or in combination.

### Semi-crystalline polymers

The semi-crystalline polymer(s) of the composition of the invention advantageously comprise a weight-average molecular mass  $M_w$  ranging from 5 000 to 1 000 000, preferably from 10 000 to 800 000 and preferentially from 15 000 to 500 000.

The semi-crystalline polymer(s) according to the invention serving as structuring agent are solids at ambient temperature (25°C) and atmospheric pressure (760 mmHg), with a melting temperature of greater than or equal to 30°C. The melting point values correspond to the melting point measured using a differential scanning calorimeter (DSC), such as the calorimeter sold under the name DSC 30 by the company Mettler, with a temperature rise of 5 or 10°C per minute (the melting point under consideration is the point corresponding to the temperature of the most endothermic peak of the thermogram).

The semi-crystalline polymer(s) according to the invention preferably have a melting temperature greater than the temperature of the keratinous support intended for receiving the said composition, in particular the skin or the lips.

The semi-crystalline polymer(s) according to the invention are capable, alone or as a mixture, of structuring the composition without the addition of a particular surfactant or of filler or of wax.

According to the invention, the semi-crystalline polymers are advantageously soluble in the fatty phase, especially to at least 1% by weight, at a temperature greater than their melting temperature.

5 Besides the crystallizable chains or blocks, the blocks of the polymers are amorphous.

For the purposes of the invention, the expression "crystallizable chain or block" means a chain or block which, if it were alone, would change  
10 from the amorphous state to the crystalline state reversibly, depending on whether one is above or below the melting temperature. For the purposes of the invention, a "chain" is a group of atoms, pendent or lateral relative to the polymer skeleton. A "block" is  
15 a group of atoms belonging to the skeleton, this group constituting one of the repeating units of the polymer.

Preferably, the polymer skeleton of the semi-crystalline polymers is soluble in the liquid fatty phase.

20 Preferably, the crystallizable blocks or chains of the semi-crystalline polymers represent at least 30% of the total weight of each polymer and better still at least 40%. The semi-crystalline polymers containing crystallizable side chains are  
25 homopolymers or copolymers. The semi-crystalline polymers of the invention containing crystallizable blocks are block or multiblock copolymers. They may be

obtained by polymerizing a monomer containing reactive (or ethylenic) double bonds or by polycondensation.

When the polymers of the invention are polymers containing crystallizable side chains, these side  
5 chains are advantageously in random or statistical form.

Preferably, the semi-crystalline polymers of the invention are of synthetic origin. Moreover, they do not comprise a polysaccharide skeleton.

10 The semi-crystalline polymers useful in the invention are in particular:

- block copolymers of polyolefins of controlled crystallization, whose monomers are described in EP-A-0 951 897,
- 15 - polycondensates, especially of aliphatic or aromatic polyester type or of aliphatic/aromatic polyester type,
- homopolymers or copolymers bearing at least one crystallizable side chain and homopolymers or  
20 copolymers bearing in the skeleton at least one crystallizable block, such as those described in document US-A-5 156 911,
- homopolymers or copolymers bearing at least one crystallizable side chain, in particular bearing fluoro  
25 group(s), as described in document WO-A-01/19333,

- and mixtures thereof. In these last two cases, the crystallizable side chain(s) or block(s) are hydrophobic.

A) *Semi-crystalline polymers containing crystallizable*  
5 *side chains*

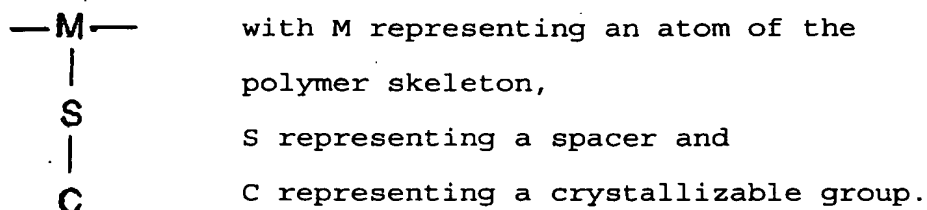
Mention may be made in particular of those defined in documents US-A-5 156 911 and WO-A-01/19333.

. They are homopolymers or copolymers comprising from 50% to 100% by weight of units resulting from the  
10 polymerization of one or more monomers bearing a crystallizable hydrophobic side chain.

. These homopolymers or copolymers are of any nature, provided that they meet the conditions mentioned hereinbelow with, in particular, the  
15 characteristic of being soluble or dispersible in the liquid fatty phase, by heating above their melting temperature mp. They can result:

- from the polymerization, especially the free-radical polymerization, of one or more monomers  
20 containing reactive or ethylenic double bond(s) with respect to a polymerization, namely a vinyl, (meth)acrylic or allylic group,
- from the polycondensation of one or more monomers bearing co-reactive groups (carboxylic acid, sulphonic  
25 acid, alcohol, amine or isocyanate), such as, for example, polyesters, polyurethanes, polyethers, polyureas or polyamides.

a) In general, the crystallizable units (chains or blocks) of semi-crystalline polymers according to the invention are derived from monomer(s) containing crystallizable block(s) or chain(s), used  
 5 for manufacturing semi-crystalline polymers. These polymers are selected especially from homopolymers and copolymers resulting from the polymerization of at least one monomer containing crystallizable chain(s) that may be represented by formula X:



10 The crystallizable chains "-S-C" may be aliphatic or aromatic, and optionally fluorinated or perfluorinated. "S" especially represents a group  $(\text{CH}_2)_n$  or  $(\text{CH}_2\text{CH}_2\text{O})_n$  or  $(\text{CH}_2\text{O})_n$ , which is linear or branched or cyclic, with n being an integer ranging from 0 to 22.  
 15 Preferably, "S" is a linear group. Preferably, "S" and "C" are different.

When the crystallizable chains are hydrocarbon-based aliphatic chains, they comprise hydrocarbon-based alkyl chains containing at least 11  
 20 carbon atoms and not more than 40 carbon atoms and better still not more than 24 carbon atoms. They are especially aliphatic chains or alkyl chains containing at least 12 carbon atoms, and they are preferably



C<sub>14</sub>-C<sub>24</sub>, preferably C<sub>16</sub>-C<sub>22</sub> alkyl chains. When they are fluoroalkyl or perfluoroalkyl chains, they contain at least 11 carbon atoms, at least 6 of which carbon atoms are fluorinated.

- 5                   As examples of semi-crystalline homopolymers or copolymers containing crystallizable chain(s), mention may be made of those resulting from the polymerization of one or more of the following monomers: saturated alkyl (meth)acrylates with the
- 10 alkyl group being C<sub>14</sub>-C<sub>24</sub>, perfluoroalkyl (meth)acrylates with a C<sub>11</sub>-C<sub>15</sub> perfluoroalkyl group, N-alkyl(meth)acrylamides with the alkyl group being C<sub>14</sub> to C<sub>24</sub> with or without a fluorine atom, vinyl esters containing alkyl or perfluoro(alkyl) chains with the alkyl group being
- 15 C<sub>14</sub> to C<sub>24</sub> (with at least 6 fluorine atoms per perfluoroalkyl chain), vinyl ethers containing alkyl or perfluoro(alkyl) chains with the alkyl group being C<sub>14</sub> to C<sub>24</sub> and at least 6 fluorine atoms per perfluoroalkyl chain, C<sub>14</sub> to C<sub>24</sub> alpha-olefins such as, for example,
- 20 octadecene, para-alkylstyrenes with an alkyl group containing from 12 to 24 carbon atoms, and mixtures thereof.

When the polymers result from a polycondensation, the hydrocarbon-based and/or

25 fluorinated crystallizable chains as defined above are borne by a monomer that may be a diacid, a diol, a diamine or a diisocyanate.

When the polymers that are the subject of the invention are copolymers, they additionally contain from 0 to 50% of groups Y or Z resulting from the copolymerization:

- 5    α) of Y, which is a polar or non-polar monomer or a mixture of the two:

    When Y is a polar monomer, it is either a monomer bearing polyoxyalkylenated groups (especially oxyethylenated and/or oxypropylenated groups), a  
10    hydroxyalkyl (meth)acrylate, for instance hydroxyethyl acrylate, (meth)acrylamide, an N-alkyl(meth)acrylamide, an N,N-dialkyl(meth)acrylamide such as, for example, N,N-diisopropylacrylamide or N-vinylpyrrolidone (NVP), N-vinylcaprolactam, a monomer bearing at least one  
15    carboxylic acid group, for instance (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid or fumaric acid, or bearing a carboxylic acid anhydride group, for instance maleic anhydride, and mixtures thereof.

    When Y is a non-polar monomer, it may be an ester  
20    of the linear, branched or cyclic alkyl (meth)acrylate type, a vinyl ester, an alkyl vinyl ether, an alpha-olefin, styrene or styrene substituted with a C<sub>1</sub> to C<sub>10</sub> alkyl group, for instance α-methylstyrene, or a macromonomer of the polyorganosiloxane type containing  
25    vinyl unsaturation.

For the purposes of the invention, the term "alkyl" means a saturated group especially of C<sub>8</sub> to C<sub>24</sub>, except where otherwise mentioned.

β) of Z, which is a polar monomer or a mixture of polar  
5 monomers. In this case, Z has the same definition as the "polar Y" defined above.

Preferably, the semi-crystalline polymers containing a crystallizable side chain are alkyl (meth)acrylate or alkyl(meth)acrylamide homopolymers  
10 with an alkyl group as defined above, and especially of C<sub>14</sub>-C<sub>24</sub>, copolymers of these monomers with a hydrophilic monomer preferably of different nature from (meth)acrylic acid, for instance N-vinylpyrrolidone or hydroxyethyl (meth)acrylate, and mixtures thereof.

15 *B) Polymers bearing in the skeleton at least one crystallizable block*

This is also a case of polymers that are soluble or dispersible in the liquid fatty phase by heating above their melting point mp. These polymers  
20 are especially block copolymers consisting of at least two blocks of different chemical nature, one of which is crystallizable.

- The polymers defined in patent US-A-5 156 911 may be used.

25 - Block copolymers of olefin or of cycloolefin containing a crystallizable chain, for instance those derived from the block polymerization of:

- cyclobutene, cyclohexene, cyclooctene, norbornene (i.e. bicyclo[2.2.1]hept-2-ene), 5-methylnorbornene, 5-ethylnorbornene, 5,6-dimethylnorbornene, 5,5,6-trimethylnorbornene, 5-ethylidenenorbornene,
- 5 5-phenylnorbornene, 5-benzylnorbornene, 5-vinylnorbornene, 1,4,5,8-dimethano-1,2,3,4,4a,5,8a-octahydronaphthalene, dicyclopentadiene, or mixtures thereof,
- with ethylene, propylene, 1-butene, 3-methyl-1-
- 10 butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene or 1-eicosene, or mixtures thereof,
- and in particular copoly(ethylene/norbornene) blocks and (ethylene/propylene/ethylidenenorbornene) block terpolymers. Those resulting from the block
- 15 copolymerization of at least 2 C<sub>2</sub>-C<sub>16</sub>, better still C<sub>2</sub>-C<sub>12</sub>,  $\alpha$ -olefins such as those mentioned above and in particular block bipolymers of ethylene and of 1-octene may also be used.
- The copolymers may be copolymers containing at
- 20 least one crystallizable block, the rest of the copolymer being amorphous (at ambient temperature). These copolymers may also contain two crystallizable blocks of different chemical nature. The preferred copolymers are those that simultaneously contain at
- 25 ambient temperature a crystallizable block and an amorphous block that are both hydrophobic and lipophilic, sequentially distributed; mention may be

made, for example, of polymers containing one of the crystallizable blocks and one of the amorphous blocks below:

- . Block that is crystallizable by nature: a)  
5 polyester, for instance poly(alkylene terephthalate)s,  
b) polyolefin, for instance polyethylenes or polypropylenes.

- . Amorphous and lipophilic block, for instance:  
amorphous polyolefins or copoly(olefin)s such as  
10 poly(isobutylene), hydrogenated polybutadiene or hydrogenated poly(isoprene).

As examples of such copolymers containing a crystallizable block and an amorphous block, mention may be made of:

- 15 α) poly( $\epsilon$ -caprolactone)-b-poly(butadiene) block copolymers, preferably used hydrogenated, such as those described in the article D6 "Melting behaviour of poly( $\epsilon$ -caprolactone)-block-polybutadiene copolymers" from S. Nojima, *Macromolecules*, 32, 3727-3734 (1999),
- 20 β) the hydrogenated block or multiblock poly(butylene terephthalate)-b-poly(isoprene) block copolymers cited in the article D7 "Study of morphological and mechanical properties of PP/PBT" by B. Boutevin et al., *Polymer Bulletin*, 34, 117-123 (1995),
- 25 γ) the poly(ethylene)-b-copoly(ethylene/propylene) block copolymers cited in the articles D8 "Morphology of semi-crystalline block copolymers of ethylene-

(ethylene-alt-propylene)" by P. Rangarajan et al.,  
Macromolecules, 26, 4640-4645 (1993) and D9 "Polymer  
aggregates with crystalline cores: the system  
poly(ethylene)-poly(ethylene-propylene)" by P. Richter  
5 et al., Macromolecules, 30, 1053-1068 (1997),  
δ) the poly(ethylene)-b-poly(ethylene) block  
copolymers cited in the general article D10  
"Crystallization in block copolymers" by I.W. Hamley,  
Advances in Polymer Science, Vol. 148, 113-137 (1999).

10               The semi-crystalline polymers in the  
composition of the invention may or may not be  
partially crosslinked, provided that the degree of  
crosslinking does not interfere with their dissolution  
or dispersion in the liquid fatty phase by heating  
15 above their melting temperature. It may then be a  
chemical crosslinking, by reaction with a  
polyfunctional monomer during the polymerization. It  
may also be a physical crosslinking which may, in this  
case, be due either to the establishment of bonds of  
20 hydrogen or dipolar type between groups borne by the  
polymer, such as, for example, the dipolar interactions  
between carboxylate ionomers, these interactions being  
of small amount and borne by the polymer skeleton; or  
to a phase separation between the crystallizable blocks  
25 and the amorphous blocks borne by the polymer.

Preferably, the semi-crystalline polymers in the composition according to the invention are non-crosslinked.

As specific examples of the structuring semi-crystalline polymer that may be used in the composition according to the invention, mention may be made of the products Intelimer® from the company Landec, described in the brochure "Intelimer® polymers", Landec IP22 (Rev. 4-97). These polymers are in solid form at ambient temperature (25°C). They bear crystallizable side chains and have the formula X above.

**Mixture of high-melting semi-crystalline polymer and low-melting semi-crystalline polymer**

In the description hereinbelow, the semi-crystalline polymer(s) with a melting temperature  $mp_2$  of less than 50°C will be referred to as "low-melting polymers" and the crystalline or semi-crystalline compound(s) with a melting temperature  $mp_1$  of greater than or equal to 50°C will be referred to as "high-melting compounds". According to the invention, the melting point may be measured especially by any known method and in particular using a differential scanning calorimeter (DSC).

The composition advantageously comprises a mixture of a polymer selected from low-melting polymers having a melting temperature of less than 50°C and of a

polymer selected from high-melting polymers having a melting temperature of at least 50°C.

According to the invention, the high-melting semi-crystalline compound(s) are advantageously  
5 polymers with a melting temperature  $mp_1$  such that  $50^\circ\text{C} \leq mp_1 \leq 150^\circ\text{C}$ , better still  $55^\circ\text{C} \leq mp_1 \leq 150^\circ\text{C}$ , and preferably  $60^\circ\text{C} \leq mp_1 \leq 130^\circ\text{C}$ , and the low-melting polymers advantageously have a melting temperature  $mp_2$  such that  
10  $30^\circ\text{C} \leq mp_2 < 50^\circ\text{C}$  and better still  $35^\circ\text{C} \leq mp_2 \leq 45^\circ\text{C}$ . This melting temperature is a first-order change of state temperature.

In general the low-melting polymers have a melting temperature  $mp_2$  at least equal to the  
15 temperature of the keratinous support intended for receiving the composition according to the invention.

As high-melting compounds that may be used in the invention, mention may be made of high-melting waxes, for instance certain polyethylene waxes such as  
20 Epolene N-14 sold by Eastman Chemical Cie., carnauba waxes and certain microcrystalline waxes, for instance those sold by Tisco under the brand name "Tisco wax 88", and also high-melting semi-crystalline polymers. Preferably, the high-melting compound is a second high-  
25 melting organic solid semi-crystalline polymer. However, it is possible to use, as high-melting compound, crystalline polymers that are solid at



ambient temperature, having a melting temperature of greater than 50°C, random polymers comprising a controlled crystallization, as described in document EP-A-0 951 897, and more particularly the commercial  
5 products Engage 8 401 and Engage 8 402 from DuPont de Nemours, with melting temperatures of 51°C and 64°C respectively, which are ethylene/1-octene random biopolymers.

i) The semi-crystalline polymers with a melting point  
10 of less than 50°C are especially those described in Examples 3, 4, 5, 7 and 9 of patent US-A-5 156 911, containing a -COOH group, resulting from the copolymerization of acrylic acid and of a C<sub>5</sub> to C<sub>16</sub> alkyl (meth)acrylate with a melting temperature ranging  
15 from 20°C to 35°C, and more particularly from the copolymerization:

- . of acrylic acid, of hexadecyl acrylate and of isodecyl acrylate in a 1/16/3 ratio,
- . of acrylic acid and of pentadecyl acrylate in a  
20 1/19 ratio,
- . of acrylic acid, of hexadecyl acrylate and of ethyl acrylate in a 2.5/76.5/20 ratio,
- . of acrylic acid, of hexadecyl acrylate and of methyl acrylate in a 5/85/10 ratio,
- 25 . of acrylic acid and of polyoctadecyl methacrylate in a 2.5/97.5 ratio.

It is also possible to use the polymer Structure "O" from National Starch, such as the product described in document US-A-5 736 125 with a melting temperature of 44°C, and also the semi-crystalline polymers with crystallizable pendent chains comprising fluoro groups, as described in Examples 1, 4, 6, 7 and 8 of document WO-A-01/19333.

It is also possible to use the low-melting semi-crystalline polymers obtained by copolymerization of stearyl acrylate and of acrylic acid or of NVP, as described in document US-A-5 519 063 or EP-A-550 745 and more especially those described in Examples 1 and 2 below, of polymer preparation.

ii) The semi-crystalline polymers with a melting point of greater than or equal to 50°C are especially the Intelimer described in the brochure "Intelimer® polymers", Landec IP22 (Rev. 4-97) with a melting temperature of 56°C, which is an impermeable, non-sticky product that is viscous at ambient temperature.

It is also possible to use semi-crystalline polymers obtained by copolymerization of behenyl acrylate and of acrylic acid or of NVP, as described in documents US-A-5 519 063 and EP-A-0 550 745, and more especially those described in Examples 3 and 4 below, of polymer preparation.

Preferably, the low-melting semi-crystalline polymers and/or those with a high melting point do not comprise a carboxylic group.

According to the invention and  
5 advantageously, the high-melting compound (crystalline or semi-crystalline) and the low-melting compound are in a weight ratio ranging from 10/90 to 90/10, better still from 40/60 to 60/40 and more preferably in a weight ratio of close to 50/50.

10 Advantageously, the weight ratio of semi-crystalline polymer having an organic structure relative to the liquid fatty phase is from 0.20 to 0.60 and better still from 0.25 to 0.50, so as to obtain a hard stick that breaks down on contact with the skin or  
15 the lips, in particular having a hardness ranging from 100 to 350 gf.

The gelation of the fatty phase may be adjusted depending on the nature of the polymer(s) and their respective concentrations, and may be such that a  
20 rigid structure in the form of a tube or a stick is obtained.

The content of each polymer is chosen according to the desired hardness of the composition and as a function of the particular application  
25 intended. The respective amounts of polymer may be such that they allow the production of a solid that can be broken down, in particular having a hardness ranging

from 100 to 350 gf. This hardness may be measured by the "cheesewire" method, which consists in cutting a tube of lipstick 12.7 mm in diameter and in measuring the hardness at 20°C, using a DFGHS 2 tensile testing machine from the company Indelco-Chatillon, travelling at a speed of 100 mm/minute. It is expressed as the shear force (expressed as gram-force) required to cut a stick under these conditions.

This hardness is such that the composition is self-supporting and can be broken down easily to form a satisfactory deposit on the skin and the lips. In addition, with this hardness, the composition of the invention in cast form, especially in the form of a stick, shows good impact strength.

The composition of the invention is preferably in the form of a solid stick with a hardness ranging from 100 gf to 350 gf, measured according to the "cheesewire" method. However, it is possible to use an amount of semi-crystalline polymer such that the composition is in the form of a soft paste that can be applied by finger or by using an applicator to keratin materials.

In practice, the total amount of semi-crystalline polymer(s) represents from 0.1% to 80%, better still from 0.5% to 40% and even better still from 3% to 30% of the total weight of the composition.

It preferably represents from 15% to 25% by weight of the composition.

The tubes or sticks according to the invention produce, after application, a glossy, non-sticky coating of uniform colour that gives good coverage (i.e. the skin or the lips do not show through the makeup).

#### **Ester**

The word "ester" according to the invention signifies a monoester.

The ester according to the invention contains 10 to 40 carbon atoms, preferably 10 to 30 carbon atoms, more preferably 12 to 26 carbon atoms and more preferably still 16 to 22 carbon atoms.

The ester according to the invention is preferably liquid at ambient temperature (25°C). It is advantageously aliphatic and/or linear.

The ester preferably represents from 10% to 40% by weight of the composition, and better still from 15% to 30%, preferably from 20% to 25%.

The ester preferably represents from 15% to 50% of the liquid fatty phase, preferably from 25% to 40%.

The weight ratio of the ester relative to the semi-crystalline polymer is advantageously between 1 and 2, preferably from 1.3 to 1.7.

The ester according to the invention may be selected from

- synthetic esters, in particular of fatty acids, such as the oils of formula  $R_1COOR_2$  in which  $R_1$  represents the residue of a higher fatty acid containing 1 to 38 carbon atoms and  $R_2$  represents a hydrocarbon chain containing 1 to 38 carbon atoms with  $39 \geq R_1 + R_2 \geq 10$ , such as, for example, purcellin oil, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate and isostearyl isostearate;
- hydroxy esters such as isostearyl lactate, octyl hydroxystearate, octyldodecyl hydroxystearate, and heptanoates, octanoates and decanoates of fatty alcohols;
- oleyl erucate;
- a C12-C15 alkyl benzoate ester (such as Finsolv TN, sold by the company Finetex),
- and mixtures thereof.

#### **Liquid fatty phase**

For the purposes of the patent application, the term "liquid fatty phase" means a fatty phase that is liquid at ambient temperature (25°C) and atmospheric pressure (760 mmHg), composed of one or more mutually compatible fatty substances that are liquid at ambient

temperature, also known as oils. This fatty phase is macroscopically homogeneous.

Advantageously, the liquid fatty phase, structured with the semi-crystalline polymers, constitutes the continuous phase of the composition. This fatty phase may contain one or more apolar or non-polar oils or a mixture of apolar oil(s) and of polar oil(s) or a mixture of polar oils, other than the aliphatic alcohol described above.

10           The apolar oils according to the invention are in particular silicone oils such as linear or cyclic polydimethylsiloxanes (PDMS) which are liquid at ambient temperature; polydimethylsiloxanes containing alkyl, alkoxy or phenyl groups, pendent and/or at the  
15 end of a silicone chain, these groups containing from 2 to 24 carbon atoms and being liquid at ambient temperature; phenyl silicones, for instance phenyl trimethicones, phenyl dimethicones, phenyl trimethylsiloxy diphenylsiloxanes, diphenyl  
20 dimethicones, diphenyl methylphenyl trisiloxanes, and 2-phenylethyl trimethylsiloxysilicates, which are liquid; linear or branched hydrocarbons or fluorocarbons of synthetic or mineral origin, which are liquid, for instance liquid paraffins and derivatives  
25 thereof, petroleum jelly, polydecenes, hydrogenated polyisobutene such as Parleam® sold by the company Nippon Oil Fats, and squalane; and mixtures thereof.

Preferably, the apolar oils used are liquid apolar oils of the hydrocarbon-based type, of mineral or synthetic origin, chosen especially from Parleam® oil (hydrogenated isoparaffin), isoparaffins and squalane, and mixtures thereof.

The liquid fatty phase advantageously comprises at least one polar oil and at least one sparingly polar oil, for instance isononyl isononanoate.

In particular, the polar oils of the invention are:

- hydrocarbon-based plant oils with a high content of triglycerides consisting of fatty acid esters (of  $C_8$  to  $C_{24}$ ) of glycerol in which the fatty acids may have varied chain lengths, these chains possibly being linear or branched, and saturated or unsaturated; these oils are, in particular, wheatgerm oil, corn oil, sunflower oil, shea butter, castor oil, sweet-almond oil, macadamia oil, apricot oil, soybean oil, rapeseed oil, cotton oil, alfalfa oil, poppy oil, pumpkin oil, sesame oil, marrow oil, avocado oil, hazelnut oil, grapeseed oil, blackcurrant seed oil, evening primrose oil, millet oil, barley oil, quinoa oil, olive oil, rye oil, safflower oil, candlenut oil, passionflower oil and musk rose oil; or alternatively caprylic/capric acid triglycerides such as those sold by the company



Stearineries Dubois or those sold under the names Miglyol 810, 812 and 818 by the company Dynamit Nobel;

- synthetic oils of formula  $R_5COOR_6$  in which  $R_5$  represents a linear or branched higher fatty acid residue containing from 7 to 40 carbon atoms and  $R_6$  represents a branched hydrocarbon-based chain containing from 3 to 40 carbon atoms, such as, for example, purcellin oil (cetostearyl octanoate), isononyl isononanoate and  $C_{12}$  to  $C_{15}$  alcohol benzoate;
- 10 - synthetic esters and ethers, for instance isopropyl myristate, 2-ethylhexyl palmitate, alcohol or polyalcohol octanoates, decanoates or ricinoleates, and hydroxylated esters, for instance isostearyl lactate or diisostearyl malate; and pentaerythritol esters;
- 15 - fatty acids containing from 12 to 22 carbon atoms such as oleic acid, linoleic acid or linolenic acid;
- mixtures thereof.

The liquid fatty phase represents, in practice, from 5% to 99% and preferably from 20% to 80% of the total weight of the composition. It advantageously represents at least 60% of the total weight of the composition.

#### Colorant

The composition advantageously comprises a colorant, which may be selected from the lipophilic dyes, hydrophilic dyes, pigments and naces usually used in cosmetic or dermatological compositions, and

mixtures thereof. This colorant is generally present in a proportion of from 0.01% to 50% (solids), and preferably from 5% to 30%, of the total weight of the composition (if present).

5           The fat-soluble dyes are, for example, Sudan Red, D&C Red 17, D&C Green 6,  $\beta$ -carotene, soybean oil, Sudan Brown, D&C Yellow 11, D&C Violet 2, D&C Orange 5, quinoline yellow and annatto. They can represent from 0% to 20% of the weight of the composition and better  
10 still from 0.01% to 6% (if present). The water-soluble dyes are, for example, beetroot juice or methylene blue, and can represent up to 6% of the total weight of the composition.

          The pigments may be white or coloured,  
15 mineral and/or organic, and coated or uncoated. Among the mineral pigments which may be mentioned are titanium dioxide or zinc dioxide, optionally surface-treated, zirconium oxide or cerium oxide, as well as iron oxides, chromium oxide, manganese violet,  
20 ultramarine blue, chromium hydrate and ferric blue. Among the organic pigments which may be mentioned are carbon black, pigments of D&C type, and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium (such as D&C Red 27, 21 or 7, D&C Yellow 5 or  
25 6 and FD&C Blue No. 1). The pigments can represent from 0 to 40% (0.01% to 40%), especially from 0.5% to 35%

and better still from 2% to 25% of the total weight of the composition (if present).

The nacreous pigments may be chosen from white nacreous pigments such as mica, especially mica  
5 coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as titanium mica with iron oxides, titanium mica with, in particular, ferric blue or chromium oxide, titanium mica with an organic pigment of the type mentioned above, and also nacreous  
10 pigments based on bismuth oxychloride. They can represent from 0% to 25% (0.05% to 25%) and better still from 0.1% to 15% of the total weight of the composition (if present).

Advantageously, the pigments and nacres are  
15 introduced into the composition in the form of a pigment paste.

For the purposes of the invention, the term "pigment paste" means a concentrated colloidal dispersion of coated or uncoated coloured particles in  
20 a continuous medium, optionally stabilized using a dispersant.

As will be appreciated, the person skilled in the art will take care to select the optional additional additives and/or the amount thereof such  
25 that the advantageous properties of the composition according to the invention are not, or are not

substantially, adversely affected by the envisaged addition.

The makeup composition of the invention may be in the form of a coloured product, in particular for the skin, optionally having care or treatment properties, and may be in particular a foundation, a blusher, a rouge, an eyeshadow, a concealer product, an eyeliner or a body makeup product; a lip makeup product, for instance a lipstick, a lipgloss or a lip pencil, optionally with care or treatment properties; a makeup product for the epidermal derivatives, for instance the nails, for the eyelashes in the form of a mascara, or for the eyebrows and the hair. It is preferably anhydrous or in cast form.

As will be appreciated, the composition of the invention must be cosmetically acceptable, i.e. it must contain a physiologically acceptable non-toxic medium and must be able to be applied to human skin, epidermal derivatives or lips of the face. For the purposes of the invention, the expression "cosmetically acceptable" means a composition of pleasant appearance, odour, feel and, where appropriate, taste.

At least one wax such as those used hitherto in cosmetics may also be used in the composition of the invention.

For the purposes of the present invention, a wax is a lipophilic fatty compound that is solid at

ambient temperature (25°C) and atmospheric pressure (760 mmHg), which undergoes a reversible solid/liquid change of state, having a melting temperature of greater than 40°C and better still greater than 50°C, 5 which may range up to 200°C, and having an anisotropic crystalline organization in the solid state. The size of the crystals is such that the crystals diffract and/or scatter light, giving the composition a cloudy, more or less opaque appearance. By bringing the wax to 10 its melting temperature, it is possible to make it miscible with oils and to form a microscopically homogeneous mixture, but, on returning the temperature of the mixture to ambient temperature, recrystallization of the wax in the oils of the mixture is 15 obtained. This recrystallization in the mixture may be responsible for the reduction in the gloss of the said mixture. Thus the composition advantageously contains little or no standard waxes, and especially less than 10% by weight and better still less than 5% of standard 20 wax relative to the total weight of the composition.

For the purposes of the patent application, the standard waxes are those generally used in cosmetology and dermatology; they are especially of natural origin, for instance beeswax, candelilla wax, 25 ouricury wax, Japan wax, cork fibre wax, sugarcane wax, paraffin wax, lignite wax, microcrystalline waxes with a melting point > 50°C, lanolin wax, montan wax,

ozokerites and hydrogenated oils such as hydrogenated jojoba oil, but also waxes of synthetic origin, for instance polyethylene waxes derived from the polymerization of ethylene, waxes obtained by Fischer-Tropsch synthesis, with a melting point  $> 50^{\circ}\text{C}$ , fatty acid esters and glycerides that are solid at  $50^{\circ}\text{C}$ , and silicone waxes, for instance alkyl- and alkoxy-poly(di)methylsiloxanes and/or poly(di)methylsiloxane esters that are solid at  $50^{\circ}\text{C}$ .

10                    Advantageously, the composition of the invention contains little or no "matting" fillers and in particular less than 5% of matting filler. This is especially the case when it is desired to obtain a glossy coating on keratin materials such as the lips, 15 the eyelashes and the hair. In contrast, fillers of this type may be used for a foundation. A matting filler is generally a filler that absorbs the skin's sweat and/or sebum, for instance silicas, talcs, clays, kaolins and polyamide powders (Nylon®).

20                    The composition according to the invention may be manufactured by the known processes generally used in cosmetology.

                    The invention further provides a cosmetic process for caring for, making up or treating human 25 keratin materials and especially human skin, facial lips and epidermal derivatives, comprising the

application of the composition, especially the cosmetic composition as defined above, to the keratin materials.

The invention further provides for the use of an ester containing 10 to 40 carbon atoms in a makeup  
5 composition comprising a) at least one liquid fatty phase structured with at least one semi-crystalline polymer having an organic structure, the melting temperature of which is greater than or equal to 30°C, and b) a colorant, the liquid fatty phase, the  
10 colorant, the ester and the polymer forming a physiologically acceptable medium.

The invention further provides for the use of a sufficient amount of an ester containing 10 to 40 carbon atoms in a composition containing a  
15 physiologically acceptable medium comprising a) at least one liquid fatty phase structured with at least one semi-crystalline polymer having an organic structure, the melting temperature of which is greater than or equal to 30°C, and b) a colorant, as an agent  
20 for imparting smoothness on application and gloss to the said composition.

The invention further provides for the use of an ester containing 10 to 40 carbon atoms in a cosmetic composition containing a physiologically acceptable  
25 medium comprising at least one liquid fatty phase structured with at least one semi-crystalline polymer

having an organic structure to obtain a composition which is smooth on application and glossy.

The invention is illustrated in greater detail in the examples that follow. The amounts are  
5 given as percentages by mass.

**I) Examples of manufacture of semi-crystalline polymers**

**Example 1: Homopolymer with a melting point of 48°C**

120 g of Parleam are introduced into a 1 l reactor equipped with a central paddle stirrer, a  
10 condenser and a thermometer, and are heated from ambient temperature to 80°C over 45 minutes. At 80°C, the mixture C<sub>1</sub> below is introduced over 2 hours:  
40 g of cyclohexane + 4 g of Trigonox 141 [2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane].  
15 30 minutes after the start of addition of the mixture C<sub>1</sub>, the mixture C<sub>2</sub> is introduced over 1 hour 30 minutes, this mixture consisting of:  
200 g of stearyl acrylate + 400 g of cyclohexane.

At the end of the two additions, the mixture  
20 is stirred for a further 3 hours at 80°C and all of the cyclohexane present in the reaction medium is then distilled off at atmospheric pressure. This gives the polymer at a concentration of 60% by weight of active substance in the Parleam.

25 Its weight-average molecular mass is of the order of 20 000-30 000 and its melting temperature T<sub>m</sub> is 48°C, measured by DSC.



**Example 2: Copolymer with a melting point of 48°C**

The same procedure as in Example 1 is applied, except that a mixture of 10 g of N-vinylpyrrolidone and 190 g of stearyl acrylate is used.

5           The polymer obtained is at a concentration of 60% by weight of active substance in Parleam, its weight-average molecular mass is 43 000-53 000 and its  $T_m$  is 48°C.

**Example 3: Homopolymer with a melting point of 58°C**

10           The same procedure as in Example 1 is applied, except that behenyl acrylate is used instead of stearyl acrylate. The polymer obtained is at a concentration of 60% by weight of active substance in Parleam. Its weight-average molecular mass is 17 000-  
15 27 000 and its  $T_m$  is 58°C.

**Example 4: Copolymer with a melting point of 58°C**

The same procedure as in Example 2 is applied, except that behenyl acrylate is used instead of stearyl acrylate. The polymer obtained is at a  
20 concentration of 60% by weight of active substance in Parleam®. Its weight-average molecular mass is 23 500-33 500 and its  $T_m$  is 58°C.

**II) Composition examples****Example 5: Lipstick formula**

25	Percentage by weight
2-Octyldodecanol	14.5
Diisostearyl malate	9.5

	Polyhydroxystearic acid	2
	Hydrogenated coco-glycerides	2
	Homopolymer prepared according to Example 1	11
	Homopolymer prepared according to Example 3	11
5	Pigments	9
	Filler	1
	Nacre	3
	Isononyl isononanoate	qs 100

10           This formula is smooth on application and as  
a coating is glossy and comfortable.